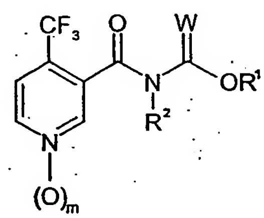
SUBSTITUTED NICOTINOYLCARBAMATES AS PESTICIDES

The invention relates to novel nicotinoylcarbamates, to their use as pesticides, preferably as insecticides and to processes for their preparation.

JP 321903/1994 and JP 101648/1998 describe amide type compounds or their salts and their use as agents for controlling harmful organisms.

The invention, accordingly, provides novel nicotinoylcarbamates of the general formula (I)



(I)

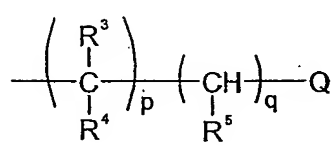
in which

m represents 0 or 1,

W represents O or S,

R^2 represents hydrogen, alkyl, alkenyl, aralkyl, cyanomethyl, alkoxycarbonylalkyl, aralkyloxycarbonyl, acyl, alkoxyalkyl or phenyl, and

R^1 represents



wherein

R^3 represents hydrogen or alkyl,

R^4 represents hydrogen, alkyl, haloalkyl, phenyl or alkoxycarbonyl,

R^5 represents hydrogen or alkyl,

p represents 0 or 1,

q represents 0 or 1, and

Q represents aryl that may be optionally substituted; 5- or 6-membered heterocyclic group that contains at least one hetero atom selected from the group consisting of N, O and S and may be optionally substituted; phenyl-substituted cycloalkyl; condensed bicyclic hydrocarbon group; trimethylsilyl; alkenyl or alkynyl.

The compounds of the formula (I), according to the present invention, have strong insecticidal activities and show good compatibility to various crops.

According to the present invention the compounds of the formula (I) surprisingly show very excellent insecticidal action compared with the similar compounds to the compounds of the formula (I), described in the prior art (e.g. JP 321903/1994 and JP 101648/1998).

In the present specification, the following definitions shall apply if no specific other definition is given:

"Halogen" represents fluoro, chloro, bromo or iodo, and preferably represents fluoro, chloro or bromo.

"Alkyl" represents a straight-chain or branched-chain C_{1-12}alkyl, for example, methyl, ethyl, n- or iso-propyl, n-, iso-, sec- or tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, etc. and preferably represents C_{1-6}alkyl.

Each alkyl part of "haloalkyl", "alkoxycarbonyl", "alkoxycarbonylalkyl" and "alkoxyalkyl" there can be mentioned the same as described in the above-mentioned "alkyl".

"Alkenyl" represents a straight-chain or branched-chain C_{2-6}alkenyl, for example, vinyl, allyl, 1-propenyl, isopropenyl, 2-butenyl, 2-pentenyl, 2-hexenyl, etc. and preferably represents C_{2-4}alkenyl.

"Alkynyl" represents a straight-chain or branched-chain C_{2-6}alkynyl, for example, ethenyl, propargyl, 1-propynyl, isopropenyl, 1- (2- or 3) butynyl, 1- (2- or 3) pentenyl, 1- (2- or 3) hexenyl, etc. and preferably represents C_{2-4}alky"nyl.

"Aryl" represents C_{6-10} aromatic hydrocarbon cyclic group, for example, phenyl, naphthyl, etc. and preferably represents phenyl.

"Aralkyl" represents, for example, benzyl, α-methylbenzyl, 2-phenylethyl, α,α-dimethylbenzyl, etc. and preferably represents benzyl.

"Heterocyclic group" represents a saturated or unsaturated 5~6-membered heterocyclic group containing at least one, preferably 1-3 hetero atoms selected from N, O and S and represents, for example, furyl, thienyl, pyrrolyl, pyrrolidinyl, tetrahydrofuryl, tetrahydrothienyl, pyrazolyl, imidazolyl, triazolyl, tetrazolyl, isoxazolyl, oxazolyl, isothiazolyl, thiazolyl, pyridyl, pyrimidinyl, piperidinyl, pyrazinyl, pyranyl, tetrahydropyranyl, tetrahydrothiopyranyl, thiopyranyl, etc.

"Condensed bicyclic hydrocarbon group" represents a condensed bicyclic C9-10 hydrocarbon group, for example, indenyl, indanyl, tetrahydronaphthyl, etc. and preferably represents indanyl or tetrahydronaphthyl.

"Aralkyl" part of "aralkyloxycarbonyl" represents the same group as described in the above-mentioned definition of "aralkyl".

"Cycloalkyl" represents C_{3-8}cycloalkyl, for example, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl or cyclooctyl, preferably represents C5-7cycloalkyl, and particularly cyclohexyl is preferable.

Preferred substituents or preferred ranges of the radicals present in the formulae (I) and the corresponding intermediate compounds are defined below.

W preferably represents O or S.

R^3 preferably represents hydrogen or C_{1-4}alkyl.

R^4 preferably represents hydrogen, C_{1-4}alkyl, halo-C_{1-4}alkyl, phenyl or C_{2-4}alkoxycarbonyl.

R^5 preferably represents hydrogen or C_{1-4}alkyl.

p preferably represents 0 or 1.

q preferably represents 0 or 1.

Q preferably represents aryl that may be optionally substituted with at least one group selected from the group consisting of C_{1-4}alkoxy, C_{1-4}alkylthio, halogen, cyano, C_{1-4}alkyl, C_{2-4} alkenyl, nitro, halo-C_{1-4}alkyl; phenoxy; phenyl that may be optionally substituted; 5~6-membered heterocyclic group containing N, O or S, 5- or 6-membered heterocyclic group that contains at least one hetero atom selected from the group consisting of N, O and S and may be optionally substituted with halo-C_{1-2}alkyl, C_{1-4}alkoxy-carbonyl or oxo; 4-phenylcyclohexyl; condensed bicyclic C_{9-10} hydrocarbon group; trimethylsilyl; C_{2-6} alkenyl; C_{2-6} alkynyl.

R^2 preferably represents hydrogen, C_{1-6}alkyl, C_{2-6}alkenyl, benzyl, cyanomethyl, C_{1-4}alkoxy-carbonyl-C_{1-4}alkyl, benzyloxycarbonyl, C_{1-4}alkylcarbonyl, C_{1-4}alkoxy-C_{1-2}alkyl or phenyl.

m preferably represents 0 or 1.

W particularly preferably represents O or S.

R^3 particularly preferably represents hydrogen or methyl.

R^4 particularly preferably represents hydrogen, methyl, trichloromethyl, trifluoromethyl, phenyl or methoxycarbonyl.

R^5 particularly preferably represents hydrogen or methyl.

p particularly preferably represents 0 or 1.

q particularly preferably represents 0 or 1.

Q particularly preferably represents phenyl which is optionally substituted with one or more groups selected from the group consisting of methoxy, methylthio, fluoro, chloro, bromo, iodo, cyano, methyl, vinyl, nitro, trifluoromethyl, phenoxy, phenyl, chloro-substituted phenyl, tolyl and

thienyl, furyl, thienyl, trifluoromethylpyrazolyl, pyridyl, trifluoromethylpyridyl, tetrahydropyranyl, tetrahydrothiopyranyl, piperidinyl, 1-(tert-butoxycarbonyl)-4-piperidinyl, pyrrolidinyltetrahydrofuryl, 1,1-dioxo-tetrahydrothiopyranyl, 4-phenylcyclohexyl, indanyl, tetrahydronaphthyl, trimethylsilyl, C_{2-4} alkenyl C_{2-4} alkynyl.

R^2 particularly preferably represents hydrogen, C_{1-4}alkyl, C_{2-4}alkenyl, benzyl, cyanomethyl, C_{1-2}alkoxy-carbonylmethyl, benzyloxycarbonyl, acetyl, C_{1-2}alkoxymethyl or phenyl.

m particularly preferably represents 0.

W very particularly preferably represents O.

R^2 very particularly preferably represents hydrogen.

R^3 very particularly preferably represents hydrogen.

R^4 very particularly preferably represents hydrogen.

The abovementioned general or preferred radical definitions apply both to the end products of the formula (I) and also, correspondingly, to the starting materials or intermediates required in each case for the preparation. These radical definitions can be combined with one another at will, i.e. including combinations between the given preferred ranges.

Preference according to the invention is given to compounds of the formula (I) which contain a combination of the meanings mentioned above as being preferred.

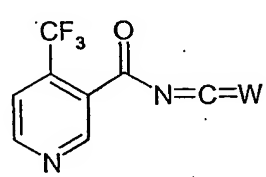
Particular preference according to the invention is given to compounds of the formula (I) which contain a combination of the meanings listed above as being particularly preferred.

Very particular preference according to the invention is given to the compounds of the formula (I) which contain a combination of the meanings listed above as being very particularly preferred..

The compounds of the formula (I) can be obtained by any of the following preparation processes a), b), c), d) or e). Particularly the compounds of the formula (I), in which R2 represents hydrogen and m represents 0, can be synthesized by the preparation processes a), b) or c), and the compounds of the formula (I), in which R2 represents another group than hydrogen and m represents 0, can be synthesized by the preparation process d), and further the compounds of the formula (I), in which m represents 1, can be synthesized by the preparation process e).

<u>Preparation process (a):</u> in case R^2 = hydrogen, m = 0:

Compounds of the formula



(II)

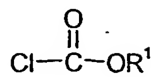
wherein W has the same definition as aforementioned, are reacted with compounds of the formula

$R^1 - OH$ (III)

wherein R^1 has the same definition as aforementioned, in the presence of inert solvents.

<u>Preparation process (b):</u> in case W = O, R^2 = hydrogen, m = 0:

4-trifluoromethylnicotinamide is reacted with compounds of the formula

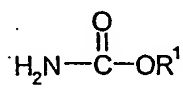


(IV)

wherein R^1 has the same definition as aforementioned, in the presence of inert solvents, and if appropriate, in the presence of a base.

<u>Preparation process (c):</u> in case W = 0, R^2 = hydrogen, m = 0:

4-trifluoromethylnicotinoyl chloride is reacted with compounds of the formula

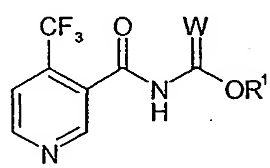


(V)

wherein R^1 has the same definition as aforementioned, in the presence of inert solvents, and if appropriate, in the presence of a base.

<u>Preparation process (d):</u> in case R^2 = as defined above, except hydrogen, m = 0:

Compounds of the formula



(Ia)

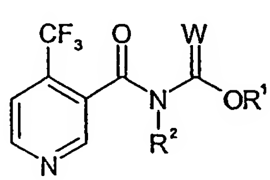
wherein W and R^1 have the same definition as aforementioned, are reacted with compounds of the formula

$R^{2'} - \mathrm{Hal}$ (VI)

wherein $R^{2'}$ is as defined above, except hydrogen and Hal represents halogen, in the presence of inert solvents, and if appropriate, in the presence of a base.

<u>Preparation process (e):</u> in case m = 1:

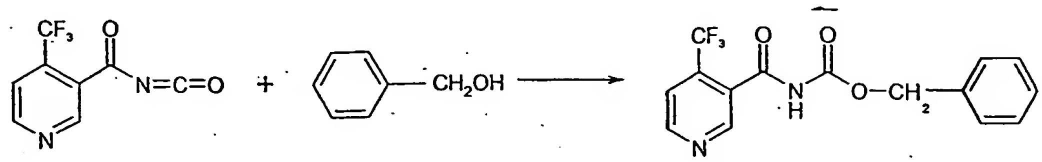
Compounds of the formula



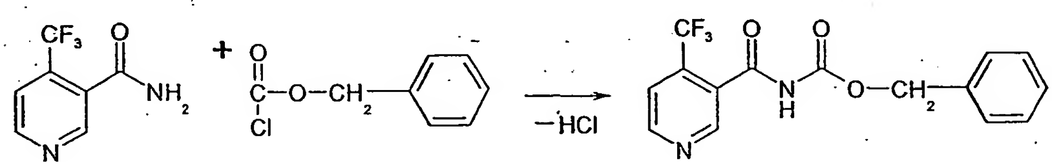
(Ie)

wherein W, R^1 and R^2 have the same definition as aforementioned, are oxidized in the presence of inert solvents.

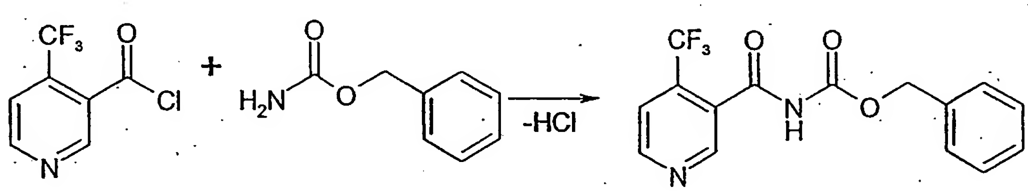
The preparation process a) to prepare compounds of the formula (I) can be illustrated by the following reaction scheme in case, for example, that 4-trifluoromethylnicotinoyl isocyanate and benzyl alcohol are used as starting materials.



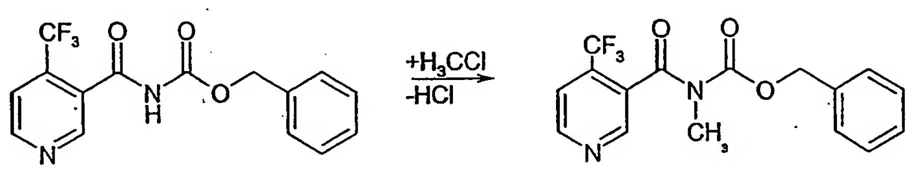
The preparation process b) to prepare compounds of the formula (I) can be illustrated by the following reaction scheme in case, for example, that 4-trifluoromethylnicotinamide and benzyl chloroformate are used as starting materials.



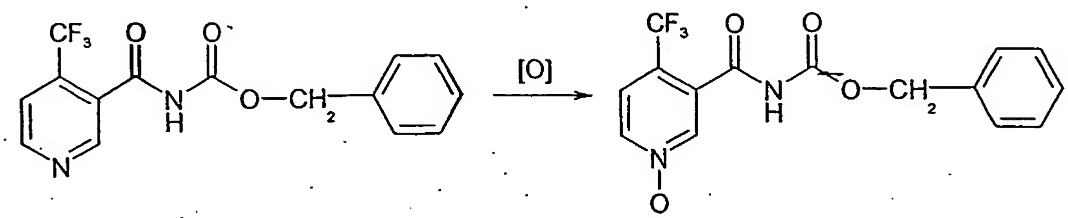
The preparation process c) to prepare compounds of the formula (I) can be illustrated by the following reaction scheme in case, for example, that 4-trifluoromethylnicotinoyl chloride and benzyl carbamate are used as starting materials.



The preparation process d) to prepare compounds of the formula (I) can be illustrated by the following reaction scheme in case, for example, that benzyl N-(4-trifluoromethyl-3-pyridylcarbonyl)carbamate and methyl chloride are used as starting materials.



The preparation process e) to prepare compounds of the formula (I) can be illustrated by the following reaction scheme in case, for example, that benzyl N-(4-trifluoromethyl-3-pyridylcarbonyl)carbamate is used as starting material and m-chloroperbenzoic acid, as oxidizing agent.



The compounds of the formula (II) in the preparation process a) can be easily obtained according to the process described in, for example, J. Med. Chem., p.1630 (1991), J. Chem. Soc., p.153 (1958).

The alcohols of formula (III) are well known in the field of organic chemistry; as their representative examples the following compounds may be mentioned: benzyl alcohol, α-methylbenzyl alcohol, phenol, 2-phenyl-isopropanol, trimethylsilylmethanol, 2-(trimethylsilyl)ethanol, 3-furylmethanol, 2-furylmethanol, 2-thienylmethanol, 2-methoxybenzyl alcohol, 3-methoxybenzyl alcohol, 4-methoxybenzyl alcohol, 4-vinylbenzyl alcohol, 4-methylthiobenzyl alcohol, 2-chlorobenzyl alcohol, 3-chlorobenzyl alcohol, 4-chlorobenzyl alcohol, 2-pyridylmethyl alcohol, 3-pyridylmethyl alcohol, 4-pyridylmethyl alcohol, 3-cyanobenzyl alcohol, trimethylsilylmethanol, 4-methylbenzyl alcohol, 2,4-dichlorobenzyl alcohol, 2,6-dichlorobenzyl alcohol, 2-bromobenzyl alcohol, 3-bromobenzyl alcohol, 4-bromobenzyl alcohol, 2-nitrobenzyl alcohol, 3-nitrobenzyl alcohol, 1-phenyl-2,2,2-trifluoroethanol, diphenylmethanol, 2-trifluoromethylbenzyl alcohol, 3-trifluoromethylbenzyl alcohol, 4-trifluoromethylbenzyl alcohol, 2-fluorobenzyl alcohol, 3-fluorobenzyl alcohol, 4-fluorobenzyl alcohol, 4-nitrobenzyl alcohol, α-methoxycarbonylbenzyl alcohol, 3-iodobenzyl alcohol, 5-trifluoromethyl-2-pyridylmethanol, 3-phenoxybenzyl alcohol, 4-phenoxybenzyl alcohol, 2-methylbenzyl alcohol, 3-methylbenzyl alcohol, 2,4-dimethylbenzyl alcohol, 4-biphenylylmethanol, 1-naphthylmethanol, 2-naphthylmethanol, 2,2-dimethyl-3-phenylpropanol, 1-phenyl-2,2,2-trichloroethanol, 2-phenethyl alcohol, 2-phenylpropanol, 1-indanyl alcohol, 2-indanyl alcohol, 1-(1,2,3,4-tetrahydronaphthyl) alcohol, 2-(1,2,3,4-tetrahydronaphthyl) alcohol, 4-tetrahydropyranyl alcohol, 4-tetrahydrothiopyranyl alcohol, 4-piperidinyl alcohol, 2-pyrrolidinyl alcohol, 3-pyrrolidinyl alcohol, 2-tetrahydrofurfuryl alcohol, 4-phenyl-cyclohexyl alcohol, 4-(2-thienyl)benzyl alcohol, 4-(4-chlorophenyl)benzyl alcohol, etc.

Among the above-mentioned alcohols, for example, 4-tetrahydrothiopyranyl alcohol, 2-(1,2,3,4-tetrahydronaphthyl) alcohol, 4-phenoxybenzyl alcohol can be easily obtained, for example, by reducing their corresponding known ketones using sodium borohydride.

4-Trifluoronicotinamide is a known compound. (c.f. JP 321903/1994.)

The chloroformic acid esters of formula (IV) are well known in the field of organic chemistry and can be easily obtained generally by reacting phosgene with the corresponding alcohols in the presence of a tertiary amine.

4-Trifluoromethylnicotinoyl chloride can be easily obtained, for example, by a reaction of known 4-trifluoromethylnicotinic acid and thionyl chloride.

The carbamic acid esters of formula (V) are well known in the field of organic chemistry and can be obtained by known processes.

The compounds of the formula (Ia) in the preparation process d) are the compounds of the formula (I) of the present invention, in case that R^2 represents hydrogen, obtained by the preparation processes a), b) (in case W = 0) or c) (in case W = 0).

The halides of formula (VI) are well known in the field of organic chemistry; as their representative examples there can be mentioned the following: chloromethyl ethyl ether, acetyl chloride, benzyl chloroformate, ethyl bromoacetate, benzyl bromide, allyl bromide, ethyl iodide, etc.

The compounds of the formula (Ie) in the preparation process e) are the compounds of the formula (I) of the present invention, in case that m = 0.

As a representative example of the oxidizing agent used for oxidation there can be mentioned m-chloroperbenzoic acid.

The aforementioned preparation process a) can be conducted, for example, according to the process described in J. Chem. Soc., p.1091 (1957) and ibid. p. 4458 (1956).

The reaction of the preparation process a) can be conducted using an adequate diluent singly or mixed. As examples of the diluent used in that case there can be mentioned aliphatic, alicyclic and aromatic hydrocarbons (may be optionally chlorinated), for example, pentane, hexane, cyclohexane, petroleum ether, ligroine, benzene, toluene, xylene, dichloromethane, chloroform, carbon tetrachloride, 1,2-dichloroethane, chlorobenzene, dichlorobenzene, etc.; ethers, for example, ethyl ether, methyl ethyl ether, isopropyl ether, butyl ether, dioxane, dimethoxyethane (DME), tetrahydrofuran (THF), diethylene glycol dimethyl ether (DGM), etc.; nitriles, for example, acetonitrile, propionitrile, acrylonitrile, etc.; acid amides, for example, dimethylformamide (DMF), dimethylacetamide (DMA), N-methylpyrrolidone, 1,3-dimethyl-2-imidazolidinone, hexamethyl phosphoric triamide (HMPA), etc.

The reaction of the preparation process a) can be conducted in a substantially wide range of temperature. However, it can be conducted in a range of generally about 0 – about 100°C, preferably about 0 – about 50°C. Although said reaction is conducted desirably under normal pressure, it can be operated optionally also under elevated pressure or under reduced pressure.

In conducting the preparation process a), the aimed compounds can be obtained, for example, by reacting 1 mole amount to a little excess amount of the compounds of the formula (III) to 1 mole of compounds of the formula (II) in a diluent, for example, 1,2-dichloroethane.

The aforementioned preparation processes b), c), d) and e) can be conducted under the similar reaction conditions by using a diluent mentioned in the above-mentioned preparation process a) except dimethylformamide.

The preparation process b) can be conducted, for example, according to the process described in J. Med. Chem., p. 2504 (1991). The preparation process c) can be conducted, for example, according to the process described in J. Chem. Soc., p. 451 (1964). The preparation process d) can be conducted, for example, according to the process described in Heterocycles, p. 373 (1987). The preparation process e) can be conducted, for example, according to the process described in J. Med. Chem., p. 2925 (1995).

The preparation processes b), c) and d) can be conducted also in the presence of a base. As a suitable base may be mentioned: carbonates of alkali metals, for example, potassium carbonate; tertiary amines, N,N-dialkylanilines and pyridines, for example, triethylamine, 1,1,4,4-tetramethylethylenediamine (TMEDA), N,N-dimethylaniline, N,N-diethylaniline, pyridine, 4-dimethylaminopyridine (DMAP), 1,4-diazabicyclo[2,2,2]octane (DABCO), 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), etc.

The compounds of the formula (I) show strong insecticidal action. The compounds of the present invention can, therefore, be used as insecticidal agents. And the active compounds of the present invention exhibit exact controlling effect against harmful insects without phytotoxicity against cultured plants. The compounds of the present invention can be used for controlling a wide variety of pests, for example, harmful sucking insects, biting insects and other plant-parasitic pests, stored grain pests, hygienic pests, etc. and applied for their extermination.

As examples of such pests there can be mentioned the following pests:

As insects, there can be mentioned coleoptera pests, for example, Callosobruchus Chinensis, Sitophilus zeamais, Tribolium castaneum, Epilachna vigintioctomaculata, Agriotes fuscicollis,

Anomala rufocuprea, Leptinotarsa decemlineata, Diabrotica spp., Manochamus alternatus, Lissorhoptrus oryzophilus, Lyctus bruneus;

Lepidoptera pests, for example,

Lymantria dispar, Malacosoma neustria, Pieris rapae, Spodoptera litura, Mamestra brassicae, Chilo suppressalis, Pyrausta nubilalis, Ephestia caütella, Adoxophyes orana, Carpocapsa pomonella, Agrotis fucosa, Galleria mellonella, Plutella maculipennis, Heliothis virescens, Phyllocnistis citrella;

Hemiptera pests, for example,

Nephotettix cincticeps, Nilaparvata lugens, Pseudococcus comstocki, Unaspis yanonensis, Myzus persicae, Aphis pomi, Aphis gossypii, Rhopalosiphum pseudobrassicas, Stephanitis nashi, Nazara spp., Cimex lectularius, Trialeurodes vaporariorum, Psylla spp.Bemisia argentifolii;

Orthoptera pests, for example,

Blatella germanica, Periplaneta americana, Gryllotalpa africana, Locusta migratoria migratoriodes;

Homoptera pests, for example,

Reticulitermes speratus, Coptotermes formosanus;

Diptera pests, for example,

Musca domestica, Aedes aegypti, Hylemia platura, Culex pipiens, Anopheles slnensis, Culex tritaeniorhynchus, etc.

Thysanoptera pests, for example, Thrips palmi Karny, Frankliniella occidentalis.

Moreover, in the field of veterinary medicine, the compounds of the present invention can be effectively used against various harmful animal-parasitic pests (endoparasites and ectoparasites), for example, insects and helminthes. As examples of such animal-parasitic pests there can be mentioned the following pests:

As insects there can be mentioned, for example,

Gastrophilus spp., Stomoxys spp., Trichodectes spp., Rhodnius spp., Ctenocephalides canis, etc.

In the present invention substances having insecticidal action against pests, which include all of them, are in some cases called as insecticides

The active compounds of the formula (I) can be made into customary formulation forms, when they are used as insecticides. As formulation forms there can be mentioned, for example, solutions, emulsifiable concentrates, wettable powders, water dispersible granules, suspensions, powders, foaming agents, pastes, tablets, granules, aerosols, active compound-impregnated natural and synthetic substances, microcapsules, seed coating agents, formulations used with burning equipment (as burning equipment, for example, fumigation and smoking cartridges, cans, coils, etc.), ULV [cold mist, warm mist], etc.

These formulations can be prepared according to per se known methods, for example, by mixing the active compounds with extenders, namely liquid diluents; liquefied gas diluents; solid diluents or carriers, and optionally by using surface-active agents, namely emulsifiers and/or dispersants and/or foam-forming agents.

In case that water is used as extender, for example, organic solvents can also be used as auxiliary solvents.

As liquid diluents or carriers there can be mentioned, for example, aromatic hydrocarbons (for example, xylene, toluene, alkylnaphthalene, etc.), chlorinated aromatic or chlorinated aliphatic hydrocarbons (for example, chlorobenzenes, ethylene chlorides, methylene chloride, etc.), aliphatic hydrocarbons [for example, cyclohexane etc. or paraffins (for example, mineral oil fractions etc.)], alcohols (for example, butanol, glycols and their ethers, esters, etc.), ketones (for example, acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, etc.), strongly polar solvents (for example, dimethylformamide, dimethyl sulfoxide, etc.), and water.

Liquefied gas diluents or carriers are substances that are gases at normal temperature and pressure and there can be mentioned, for example, aerosol propellants such as butane, propane, nitrogen gas, carbon dioxide, halogenated hydrocarbons.

As solid diluents there can be mentioned, for example, ground natural minerals (for example, kaolin, clay, talc, chalk, quartz, attapulgite, montmorillonite, diatomaceous earth, etc.), ground synthetic minerals (for example, highly dispersed silicic acid, alumina, silicates, etc.), etc.

As solid carriers for granules there can be mentioned, for example, crushed and fractionated rocks (for example, calcite, marble, pumice, sepiolite, dolomite, etc.) synthetic granules of inorganic and organic meals, particles of organic materials (for example, saw dust, coconut shells, maize cobs, tobacco stalks, etc.) etc.

As emulsifiers and/or foam-forming agents there can be mentioned, for example, nonionic and anionic emulsifiers [for example, polyoxyethylene fatty acid esters, polyoxyethylene fatty acid

alcohol ethers (for example, alkylaryl polyglycol ethers), alkylsulfonates, alkylsulfates, arylsulfonates, etc.], albumin hydrolysis products, etc.

Dispersants include, for example, lignin sulfite waste liquor, methyl cellulose, etc.

Tackifiers can also be used in formulations (powders, granules, emulsifiable concentrates). As said tackifiers there can be mentioned, for example, carboxymethyl cellulose, natural and synthetic polymers (for example, gum Arabic, polyvinyl alcohol, polyvinyl acetate, etc.) etc.

Colorants can also be used. As said colorants there can be mentioned, for example, inorganic pigments (for example, iron oxide, titanium oxide, Prussian Blue, etc,), organic dyestuffs such as alizarin dyestuffs, azo dyestuffs or metal phthalocyanine dyestuffs, and further traces nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

Said formulations can contain the aforementioned active components of the amount in the range of generally 0.1-95 % by weight, preferably 0.5-90 % by weight.

The active compounds of the formula (I) of the present invention can exist also as a mixed agent with other active compounds, for example, insecticides, poisonous baits, bactericides, miticides, nematicides, fungicides, growth regulators, herbicides, etc. in the form of their commercially useful formulations and in the application forms prepared from such formulations. Here, as the above-mentioned insecticides, there can be mentioned, for example, organophosphorous agents, carbamate agents, carboxylate type chemicals, chlorinated hydrocarbon type chemicals, insecticidal substances produced by microbes, etc.

Further, the active compounds of the formula (I) can exist also as a mixed agent with a synergist and as such formulations and application forms commercially useful ones can be mentioned. Said synergist itself must not be active, but is a compound that enhances the action of the active compound.

The content of the active compounds of the formula (I) in a commercially useful application form can be varied in a wide range.

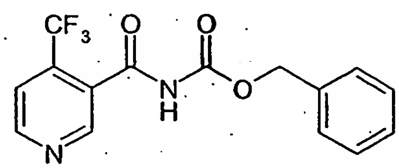
The concentration of the active compounds of the formula (I) at the time of application can be, for example, in the range of 0.0000001-100 % by weight, preferably in the range of 0.00001-1 % by weight.

The compounds of the formula (I) can be used by usual methods suitable to the application forms.

In case of application against hygienic pests and stored grain pests the active compounds of the present invention have a good stability against alkali on calcific substances and further show an excellent residual effectiveness in wood and soil.

Then the present invention will be described more specifically by examples. The present invention, however, should not be restricted only to them in any way.

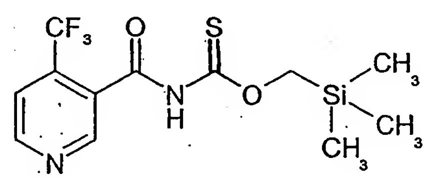
Synthesis Example 1



After oxalyl chloride (0.14 ml) was added to a suspension of 4-trifluoromethyl-nicotinamide (0.2 g) in 1,2-dichloroethane (10 ml) at room temperature, the mixture was refluxed for 2 hours. The solvent was distilled off under reduced pressure and the residue was dissolved in methylene chloride. Benzyl alcohol (0.11 g) was added to the solution and the mixture was stirred at room temperature for 2 hours. The solvent was distilled off under reduced pressure and the residue was separated and purified by silica gel column chromatography (hexane: ethyl acetate = 3:1) to obtain benzyl N-(4-trifluoromethyl-3-pyridylcarbonyl)carbamate (0.24 g).

1H-NMR: 8.85 (1H, d), 8.72 (1H, s), 7.94 (1H,brs), 7.56 (1H, d), 7.4-7.2 (5H, m), 5.11 (2H, s)

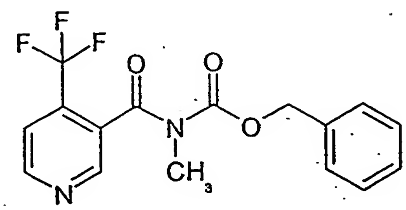
Synthesis Example 2



To a methylene chloride solution of 4-trifluoromethyl-nicotinic acid (1g) and catalytic amount of N,N-dimethylformamide, oxalyl chloride (0.5 ml) was added and the mixture was stirred at room temperature for 1 hour. The solvent was distilled off under reduced pressure and the residue was dissolved in toluene. Potassium carbonate (0.5 g) and tetrabutylammonium thiocyanate (1.89 g) were added to the solution and the mixture was stirred for 30 minutes. Then trimethylsilylmethanol (0.66 g) was added thereto and the mixture was stirred at room temperature for 1 hour. After diluting the reaction mixture with ethyl acetate, it was washed with water, 1N hydrochloric acid and saturated aqueous solution of sodium chloride and the organic layer was dried with magne-

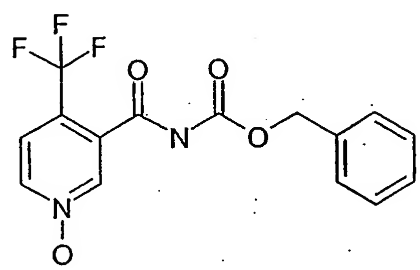
sium sulfate. The solvent was distilled off under reduced pressure and the residue was separated and purified by silica gel column chromatography (hexane: ethyl acetate = 5:1) to obtain trimetyl-silanylmethyl N-(4-trifluoromethyl-3-pyridylcarbonyl)thiocarbamate (0.77 g). mp: 105-107°C

Synthesis Example 3



60 % Sodium hydride (36 mg) was suspended in N,N-dimethylformamide and N,N-dimethylformamide solution of benzyl N-(4-trifluoromethyl-3-pyridylcarbonyl)carbamate (0.4 g) was slowly added thereto. After stirring the mixture at room temperature for 30 minutes, methyl iodide (0.35 g) was added thereto and the mixture was stirred at room temperature for 1 hour. The reaction mixture was diluted with ethyl acetate, washed with saturated aqueous solution of sodium chloride and the organic layer was dried with magnesium sulfate. The solvent was distilled off under reduced pressure and the residue was separated and purified by silica gel column chromatography (hexane: ethyl acetate = 6:1) to obtain benzyl N-methyl-N-(4-trifluoromethyl-3-pyridylcarbonyl)carbamate (0.33 g). n_D^{20}: 1.5185

Synthesis Example 4

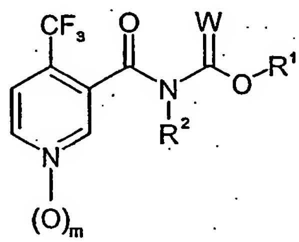


m-Chloroperbenzoic acid (0.27 g) was slowly added to a methylene chloride solution of benzyl N-(4-trifluoromethyl-3-pyridylcarbonyl)carbamate (0.3 g). After stirring at room temperature for 12 hours, the reaction solution was washed with saturated aqueous solution of sodium hydrogen carbonate and saturated aqueous solution of sodium chloride, and the organic layer was dried with magnesium sulfate. The solvent was distilled off under reduced pressure and the obtained crystals were recrystallized from toluene to obtain benzyl (1-oxy-4-trifluoromethyl-3-pyridylcarbonyl)-carbamate (0.18 g). mp: 204-205°C

The compounds of the formula (I) of the present invention obtained by the similar processes to the above-mentioned Synthesis Examples are shown in the following Table 1, together with the compounds shown in the above-mentioned Synthesis Examples.

In the Table, Ph represents phenyl, Me represents methyl, Et represents ethyl, tert-Bu represents tert-butyl, Fu represents furyl, Th represents thienyl, Py represents pyridyl, Nap represents naphthyl, Pyz represents pyrazolyl, Pip represents piperidinyl, Pyrr represents pyrrolidinyl and c-Hex represents cyclohexyl.

Table 1



Cpd No.	W	R²	R¹	m	mp.°C/ n_D^{20}/NMR
1	O	H	CH_2Ph	0	a
2	O	H	Ph	0	b
3	O	H	$CH(CH_3)Ph$	0	116-118
4	O	H	$C(CH_3)_2Ph$	0	140-141
5	O	H	$CH_2CH_2Si(CH_3)_3$	0	107-108
6	O	H	CH_2(3-Fu)	0	105-106
7	O	H	CH_2(2-Fu)	0	85-87
8	O	H	CH_2(2-Th)	0	116-117
9	O	H	CH_2(3-Th)	0	90-92
10	O	H	CH_2(2-MeO-Ph)	0	101-104
11	O	H	CH_2(3-MeO-Ph)	0	122-124
12	O	H	CH_2(4-MeS-Ph)	0	101-103
13	O	H	CH_2(4-MeO-Ph)	0	118-119
14	O	H	CH_2(2-Cl-Ph)	0	133-135
15	O	H	CH_2(3-Cl-Ph)	0	92-97
16	O	H	CH_2(4-Cl-Ph)	0	113-114
17	O	H	CH_2(2-Py)	0	1.5240
18	O	H	CH_2(3-Py)	0	156-157

Cpd No.	W	R^2	R^1	m	mp.°C/ n_D^{20}/NMR
19	O	H	CH_2(4-Py)	0	91-106
20	O	H	CH_2(3-CN-Ph)	0	121-122
21	O	CH_2CN	CH_2Ph	0	90-93
22	O	CH_3	CH_2Ph	0	1.5185
23	O	CH_2CH_3	CH_2Ph	0	1.5190
24	O	$CH_2CH{=}CH_2$	CH_2Ph	0	1.5185
25	O	CH_2Ph	CH_2Ph	0	1.5490
26	O	CH_2CO_2Et	CH_2Ph	0	1.5063
27	O	CO_2CH_2Ph	CH_2Ph	0	1.5445
28	O	H	$CH_2Si(CH_3)_3$	0	97-99
29	O	H	CH_2(4-Me-Ph)	0	c
30	O	H	CH_2(2,4-diCl-Ph)	0	158-160
31	O	H	CH_2(2,6-diCl-Ph)	0	154-156
32	O	H	CH_2(2-Br-Ph)	0	d
33	O	H	CH_2(2-NO_2-Ph)	0	e
34	O	H	CH_2(3-NO_2-Ph)	0	121-122
35	O	H	$CH(CF_3)Ph$	0	84-91
36	O	H	CH(Ph)Ph	0	121-122
37	O	H	CH_2(2-CF_3-Ph)	0	127-130
38	O	H	CH_2(3-CF_3-Ph)	0	96
39	O	H	CH_2(4-CF_3-Ph)	0	132-133
40	O	H	CH_2(2-F-Ph)	0	97-100
41	O	H	CH_2(3-F-Ph)	0	114-115
42	O	H	CH_2(4-F-Ph)	0	130-133
43	O	H	CH_2(4-NO_2-Ph)	0	f
44	O	H	$CH(CO_2Me)Ph$	0	55-61
45	O	H	CH_2(3-I-Ph)	0	g
46	O	H	CH_2(2-(5-CF_3-Py))	0	h
47	O	$COCH_3$	CH_2Ph	0	i
48	O	CH_2OEt	CH_2Ph	0	1.5085
49	O	H	CH_2(3-Ph-0-Ph)	0	88-91
50	O	H	CH_2(2-Me-Ph)	0	129-130
51	O	H	CH_2(3-Me-Ph)	0	113-114

Cpd No.	W	R^2	R^1	m	mp.°C/ n_D^{20}/NMR
52	O	H	CH_2(2,4-diMe-Ph)	0	120-121
53	O	H	CH_2(2,4,6-triMe-Ph)	0	179-180
54	O	H	CH_2(4-Ph-Ph)	0	124-125
55	O	H	CH_2(1-Nap)	0	147-148
56	O	H	CH_2(2-Nap)	0	115-117
57	O	H	$CH(C(CH_3)_3)Ph$	0	165-166
58	O	H	$CH(CCl_3)Ph$	0	j
59	O	H	CH_2CH_2Ph	0	85-86
60	O	H	$CH_2CH(CH_3)Ph$	0	109-111
61	O	H	CH_2(4-tert-Bu-Ph)	0	153-155
62	O	H	1-indanyl	0	144-146
63	O	H	2-indanyl	0	148-151
64	O	H	1-(1,2,3,4-tetrahydro-Nap)	0	142-145
65	O	H	2-(1,2,3,4-tetrahydro-Nap)	0	163-171
66	O	H	4-tetrahydropyranyl	0	1.4801
67	O	H	4-tetrahydrothiopyranyl	0	1.4974
68	O	H	4-Pip	0	k
69	O	H	CH_2(3-tetrahydro-Fu)	0	82-89
70	O	H	CH_2(2-tetrahydro-Fu)	0	1.4909
71	O	H	CH_2(2-tetrahydropyranyl)	0	1.4890
72	O	H	3-tetrahydro-Fu	0	103-111
73	O	H	CH_2(1-(3-CF_3-Pyz))	0	110-113
74	O	H	CH_2(2-Ph-Ph)	0	140-142
75	O	H	CH_2(3-Ph-Ph)	0	82-88
76	O	H	CH_2(4-(3'-MeO-Ph)-Ph)	0	161-163
77	O	H	CH_2(4-(2'-Me-Ph)-Ph)	0	119-121
78	O	H	Ph	0	
79	O	H	$CH_2Si(CH_3)_3$	0	
80	O	H	CH_2Ph	0	
81	O	H	CH_2Ph	1	204-205
82	O	H	CH_2(3-Br-Ph)	0	100-103
83	O	H	CH_2(4-Br-Ph)	0	115-119
84	O	H	4-(1,1-dioxo-tetrahydro-	0	

Cpd No.	W	R^2	R^1	m	mp.°C/ n_D^{20}/NMR
			thiopyranyl)		
85	O	H	2-Pyrr	0	
86	O	H	3-Pyrr	0	
87	O	H	CH_2(4-Ph-O-Ph)	0	1.5549
88	S	H	$CH_2Si(CH_3)_3$	0	105-107
89	O	H	CH_2(4-vinyl-Ph)		91-93
90	O	H	4-Ph-C-Hex	0	l
91	O	H	CH_2(4-(2-Th)-Ph)	0	142-143
92	O	H	CH_2(4-(4-Cl-Ph)-Ph)	0	165-168
93	O	H	4-(1-tert-Bu-OCO)Pip	0	98-110
94	O	H	CH_2-C≡CH	0	m
95	O	H	$CH(CH_3)$-C≡CH	0	n
96	O	H	$C(CH_3)_2$-C≡CH	0	o
97	O	H	$C(CH_3)(C_2H_5)$C≡CH	0	p
98	O	H	$CH_2C{\equiv}CCH_3$	0	q
99	O	H	$CH_2C{\equiv}CCH_2CH_3$	0	r
100	O	CH_2Ph	$CH_2CH{=}CH_2$	0	s
101	O	H	$CH_2CH{=}CH_2$	0	t

Fu = Furanyl, Th = Thienyl, PH = Phenyl, Py = Pyrridyl, Pyrr = Pyrrolyl

[1]H-NMR values mentioned as a-l in the above-mentioned Table 1 are as follows (chemical shift δ in ppm):

a	8.85(1H,d), 8.72(1H,s), 7.94(1H,brs), 7.56(1H,d), 7.4-7.2(5H,m), 5.11(2H,s)
b	8.87(1H,d), 8.80(1H,s), 8.38(1H,brs), 7.59(1H,d), 7.4-7.2(3H,m), 7.1-7.0(2H,m)
c	8.83(1H,d), 8.70(1H,s), 8.25(1H,brs), 7.55(1H,d), 7.3-7.2(4H,m), 5.06(2H,s), 2.36(3H,s)
d	8.84(1H,d), 8.74(1H,s), 7.96(1H,brs), 7.6-7.5(2H,m), 7.4-7.2(4H,m), 5.21(2H,s)
e	8.87(1H,d), 8.76(1H,s), 8.42(1H,brs), 8.13(1H,d), 7.7-7.5(4H,m), 5.57(2H,s)
f	8.88(1H,d), 8.74(1H,s), 8.23(2H,d), 8.14(1H,brs), 7.60(1H,d), 7.47(2H,d), 5.23(2H,s)
g	8.87(1H,d), 8.73(1H,s), 8.08(1H,brs), 7.7-7.5(3H,m), 7.3-7.2(1H,m), 7.10(1H,t), 5.04(2H,s)
h	9.11(1H,brs), 8.9-8.8(2H,m), 8.76(1H,s), 8,0-7.9(1H,m), 7.58(1H,d), 7,44(1H,d), 5.31(2H,s)
i	8.82(1H,d), 8.78(1H,s), 7.50(1H,d), 7.4-7.3(3H,m), 7.2-7.1(2H,m), 5.16(2H,s)
j	9.11(1H,Brs), 8.90(1H,d), 8.75(1H,s), 7.60(1H,d), 7.5-7.3(5H,m), 6.20(1H,s)
k	8.87(1H,d), 8.73(1H,s), 7.59(1H,d), 4.9-4.7(1H,m), 3,5-2.6(5H,m), 2,0-1.8(2H,m), 1.7-1.5(2H,m)

l	9.0-8.7(2H,m), 8.0-7.8(1H,m), 7.6-7.5(1H,m), 7.4-7.1(5H,m), 5.1-4.6(1H,m), 2.6-1.4(10H,m)
m	8.89 (1H, d), 8.75 (1H, s), 8.22 (1H, s), 7.61 (1H, d), 4.71 (2H, d), 2.53 (1H, t)
n	8.89 (1H, d), 8.75 (1H, s), 8.09 (1H, s), 7.60 (1H, d), 5.31 (1H, ddd), 2.51 (1H, q), 1.49 (3H, dd)
o	8.87 (1H, d), 8.74 (1H, s), 7.86 (1H, s), 7.59 (1H, d), 2.55 (1H, s), 1.63 (6H, s)
p	8.87 (1H, d), 8.74 (1H, s), 7.80 (1H, s), 7.59 (1H, t), 2.56 (1H, s), 1.86 (2H, ddd), 1.62 (3H, s), 0.99 (3H, t)
q	8.89 (1H, dd), 8.74 (1H, s), 8.05 (1H, s), 7.60 (1H, d), 4.66 (2H, q), 1.85 (3H, t)
r	8.88 (1H, d), 8.74 (1H, s), 8.03 (1H, s), 7.60 (1H, d), 4.68 (2H, t), 2.21 (2H, tt), 1.13 (3H, t)
s	8.88 (1H, d), 8.74 (1H, s), 8.19 (1H, s), 7.60 (1H, d), 5.84 (1H, tt), 5.35-5.26 (2H, m), 4.59 (2H, dt)
t	8.79 (1H, dd), 8.57 (1H, s), 7.54 (1H, d), 7.43-7.28 (5H, m), 5.61-5.50 (1H, m), 5.17-5.08 (4H, m), 4.45 (2H, dt)

Biological Test Example 1:

Test against *Myzus persicae** resistant to organophosphorous agents and carbamates

Preparation of test solution: Solvent: Dimethylformamide 7 parts by weight; Emulsifier: Polyoxyethylene alkyl phenyl ether 3 part by weight

In order to make an appropriate formulation of an active compound 1 part by weight of the active compound was dissolved in the above-mentioned amount of solvent containing the above-mentioned amount of emulsifier and the solution was diluted with water to a prescribed concentration.

Test method: About 30 bred *Myzus persicae** resistant to organophosphorous agents and carbamates were inoculated per 1 seedling of eggplant planted in a vinyl pot of 6cm diameter. One day after the inoculation, a sufficient amount of a diluted aqueous solution of a prescribed concentration of an active compound prepared as mentioned above, was sprayed by using a spray gun. After spraying it was placed in a green house of 28°C and the rate of death was calculated 7 days after the spraying. Test was repeated twice.

Results: The compounds No. 1, 3, 5, 6, 8, 9, 14, 18, 23, 29, 33, 35, 38, 40, 44, 54, 55, 59, 62, 70, 73, 84 offered to the test as specific examples showed 100% of rate of death at 100ppm concentration of the effective component.

Formulation Example 1 (Granule)

To a mixture of 10 parts of the compound of the present invention (No. 1), 30 parts of bentonite (montmorillonite), 58 parts of talc and 2 parts of ligninsulfonate salt, 25 parts of water are added, well kneaded, made into granules of 10-40 mesh by an extrusion granulator and dried at 40-50°C to obtain granules.

Formulation Example 2 (Granules)

95 Parts of clay mineral particles having particle diameter distribution in the range of 0.2-2mm are put in a rotary mixer. While rotating it, 5 parts of the compound of the present invention (No. 1) are sprayed together with a liquid diluent, wetted uniformly and dried at 40-50°C to obtain granules.

Formulation Example 3 (Emulsifiable concentrate)

30 Parts of the compound of the present invention (No. 1), 55 parts of xylene, 8 parts of polyoxyethylene alkyl phenyl ether and 7 parts of calcium alkylbenzenesulfonate are mixed and stirred to obtain an emulsifiable concentrate.

Formulation Example 4 (Wettable powder)

15 Parts of the compound of the present invention (No. 1), 80 parts of a mixture of white carbon (hydrous amorphous silicon oxide fine powder) and powder clay (1:5), 2 parts of sodium alkylbenzenesulfonate and 3 parts of sodium alkylnaphthalenesulfonate-formalin-condensate are crushed and mixed to make a wettable powder.

Formulation Example 5 (Water dispersible granule)

20 Parts of the compound of the present invention (No. 1), 30 parts of sodium ligninsulfonate, 15 parts of bentonite and 35 parts of calcined diatomaceous earth powder are well mixed, added with water, extruded with 0.3mm screen and dried to obtain water dispersible granules.